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**(54) Title of the Invention :**

**Low Crystallinity Ethylene Type Random Co-polymer, its Production Method and its Usage**

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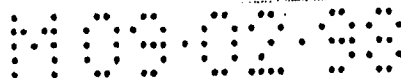
**Description**

**1. Title of the Invention :**

**Low Crystallinity Ethylene Type Random Co-polymer, its Production Method and its Usage**

**2. Scope of the Patent Application**

1) Low crystallinity ethylene type random co-polymer made out of ethylene and an  $\alpha$  -



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olefin with 3 to 20 carbon atoms, and which is characterized by the fact that:

(a) the content of the ethylene component is in the range of 35 to 85 wt %, and the content of the  $\alpha$  - olefin component is 15 to 65 wt %;

(b) the intrinsic viscosity  $[\eta]$  measured in decalin at 135 °C is in the range of 0.5 to 10 dL / g,;

(c) the molecular weight distribution ( $M_w / M_n$ ) obtained by gel permeation chromatography is less than 2.5,;

(d) the crystallization degree that was obtained by X - ray diffraction is 30 % or lower,;

(e) the value of B that can be indicated by the following equation (I), is in the range that it can satisfy the following equation (II),

$$B \equiv (P_{OE}) / (2 P_O \cdot P_E) \quad (I)$$

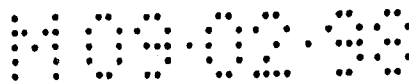
[In the equation,  $P_E$  indicates the mole ratio content of the ethylene component in the co-polymer,  $P_O$  indicates the mole ratio content of the  $\alpha$  - olefin component, and  $P_{OE}$  indicates the mole ratio of the  $\alpha$  - olefin - ethylene chain of the entire diad chain.]

$$1.05 \leq B \leq 2 \quad (II)$$

(f) in the  $^{13}\text{C}$  - NMR spectrum, the  $\alpha\beta$  signal and the  $\beta\gamma$  signal based on the methylene chain between two adjoining tertiary carbon atoms in the co-polymer main chain, can not be seen, and

(g) the part which can be dissolved in boiling methyl acetate is 2 wt % or less.

2) Method to produce the low crystallinity ethylene type random co-polymer made out



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of ethylene and an  $\alpha$  - olefin with 3 to 20 carbon atoms which can be explained by the following (a) to (g), and this method is characterized by the fact that the ethylene and the  $\alpha$  - olefin with 3 to 20 carbon atoms are co-polymerized in the presence of a catalyst which consists of:

(A) a zirconium hydride compound in which the ligand is a group with a conjugated  $\pi$  electron, and

(B) aluminoxane.

(a) the content of the ethylene component is in the range of 35 to 85 wt %, and the content of the  $\alpha$  - olefin component is 15 to 65 wt %;

(b) the intrinsic viscosity  $[\eta]$  measured in decalin at 135 °C is in the range of 0.5 to 10 dL / g.;

(c) the molecular weight distribution ( $M_w / M_n$ ) obtained by gel permeation chromatography is less than 2.5.;

(d) the crystallization degree that was obtained by X - ray diffraction is 30 % or lower.;

(e) the value of B that can be indicated by the following equation ( I ), is in the range that it can satisfy the following equation ( II ),

$$B \equiv ( P_{OE} ) / ( 2 P_O \cdot P_E ) \quad ( I )$$

[In the equation,  $P_E$  indicates the mole ratio content of the ethylene component in the co-polymer,  $P_O$  indicates the mole ratio content of the  $\alpha$  - olefin component, and  $P_{OE}$  indicates the mole ratio of the  $\alpha$  - olefin - ethylene chain of the entire diad chain.]

$$1.05 \leq B \leq 2 \quad ( II )$$

(f) in the  $^{13}\text{C}$  - NMR spectrum, the  $\alpha\beta$  signal and the  $\beta\gamma$  signal based on the methylene

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chain between two adjoining tertiary carbon atoms in the co-polymer main chain, can not be seen, and

(g) the part which can be dissolved in boiling methyl acetate is 2.0 wt % or less.

3) The blending agent for the thermo plastic resin which consists of the low crystallinity ethylene type random co-polymer made out of ethylene and an  $\alpha$  - olefin with 3 to 20 carbon atoms which can be explained by the following (a) to (g),

(a) the content of the ethylene component is in the range of 35 to 85 wt %, and the content of the  $\alpha$  - olefin component is 15 to 65 wt %;

(b) the intrinsic viscosity  $[\eta]$  measured in decalin at 135 °C is in the range of 0.5 to 10 dL / g,;

(c) the molecular weight distribution ( $M_w / M_n$ ) obtained by gel permeation chromatography is less than 2.5,;

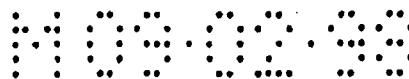
(d) the crystallization degree that was obtained by X - ray diffraction is 30 % or lower,;

(e) the value of B that can be indicated by the following equation ( I ), is in the range that it can satisfy the following equation ( II ),

$$B \equiv (P_{OE}) / (2 P_O \cdot P_E) \quad (I)$$

[In the equation,  $P_E$  indicates the mole ratio content of the ethylene component in the co-polymer,  $P_O$  indicates the mole ratio content of the  $\alpha$  - olefin component, and  $P_{OE}$  indicates the mole ratio of the  $\alpha$  - olefin · ethylene chain of the entire diad chain.]

$$1.05 \leq B \leq 2 \quad (II)$$



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(f) in the  $^{13}\text{C}$  - NMR spectrum, the  $\alpha\beta$  signal and the  $\beta\gamma$  signal based on the methylene chain between two adjoining tertiary carbon atoms in the co-polymer main chain, can not be seen, and

(g) the part which can be dissolved in boiling methyl acetate is 2.0 wt % or less.

### 3. Detailed Explanation of the Invention

#### [Field of Utilization in Industry]

This invention relates to the low crystallinity ethylene type random co-polymer, its production method and its usage. To be specific, it relates to the low crystallinity ethylene type random co-polymer of which the molecular weight distribution and the composition distribution are narrow, and which has excellent transparency, a non-sticky surface and excellent dynamic physical properties, and its production method and its usage.

#### [Existing Technique]

The low crystallinity ethylene  $\cdot \alpha$  - olefin co-polymer has been used for the soft forming usage or as various resin reformers, and the demand for it has been increasing recently. The production method that is known is such that ethylene and the  $\alpha$  - olefin are co-polymerized in the presence of a titanium type catalyst comprised of a titanium compound and an organic aluminum compound, or a vanadium type catalyst comprised of a vanadium compound and an organic aluminum compound. The low crystallinity ethylene  $\cdot \alpha$  - olefin co-polymer that can be obtained by the titanium type catalyst, usually has a wide molecular weight distribution and a wide composition distribution, and it used to have poor transparency, poor surface non-stickiness and poor dynamic physical properties. Compared with those that can be obtained with a titanium type catalyst, the low crystallinity ethylene  $\cdot \alpha$  - olefin co-polymer that can be obtained with a vanadium type catalyst have a narrower molecular weight distribution and a narrower

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composition distribution. Also, the transparency, surface non-stickiness and the dynamic physical properties are much improved, however, it is still not sufficient for the usages in which these performances are required, and the low crystallinity ethylene -  $\alpha$  - olefin co-polymer in which these performances are further improved, has been requested.

On the other hand, the catalyst comprised of a zirconium compound and aluminoxane has been collecting attention as the Ziegler type olefin polymerization catalyst.

Patent Application Kokai No. S58-19309 described the method to polymerize ethylene and one or two  $\alpha$  - olefins with  $C_3$  to  $C_{12}$  at a temperature of - 50 °C to 200 °C, in the presence of the catalyst that was comprised of:

the transition metal- containing compound that can be indicated by the following formula;



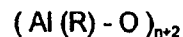
[Here, R is cyclo penta dienyl,  $C_1$  to  $C_6$  - alkyl, halogen. Me is the transition metal and Hal is a halogen.]

and the linear aluminoxane that can be indicated by the following formula;



[Here, R is methyl or ethyl. n is a number from 4 to 20.]

or the cyclic aluminoxane that can be indicated by the following formula;



[Here, R and n are the same as in the above description.]

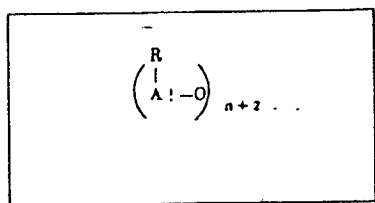
The same Kokai Official Gazette indicates that in order to adjust the density of the poly

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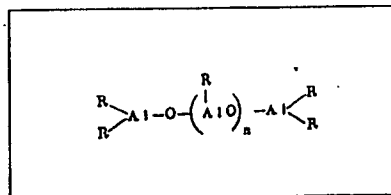
ethylene that is going to be obtained, the ethylene should be polymerized in the presence of a small amount, up to 10 wt %, of an  $\alpha$  - olefin with a slightly long chain or a mixture.

Patent Application Kokai No. S59-95292 shows the invention related to the method to produce the linear aluminoxane that can be indicated by the following formula;



[Here, n is 2 to 40, and R is C<sub>1</sub> to C<sub>6</sub> - alkyl.]

and the cyclic aluminoxane that can be indicated by the following formula;



[Here, the definitions of R and n are the same as in the above description.]

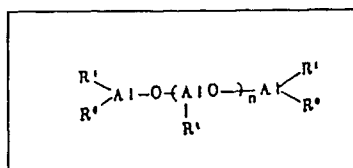
The same report says that, when the olefin is polymerized by mixing, for example, the

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methyl aluminoxane that was produced by this method, and the bis (cyclo penta dienyl) compound of titanium or zirconium, 25 million g or more of poly ethylene can be obtained per 1 g of transition metal per hour.

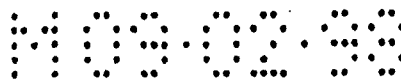
Patent Application Kokai No. S60-35005 shows the method to produce the olefin polymerization catalyst, in which the aluminoxane compound that can be indicated by the following formula;



[Here, R<sup>1</sup> is a C<sub>1</sub> to C<sub>10</sub> -alkyl. R<sup>0</sup> can be R<sup>1</sup> or it bonds and indicates -O-.]

is reacted first with magnesium, and then the reaction product is chlorinated, and then it is treated with the compound of Ti, V, Zr or Cr. The same Official Gazette says that the above mentioned catalyst is especially suitable for the co-polymerization of the mixture of ethylene and a C<sub>3</sub> to C<sub>12</sub> - α - olefin.

Patent Application Kokai No. S60-35006 shows the combination of (a) the mono-, di-, or tri- cyclo penta dienyl of two or more transition metals or their derivatives, and (b) alumoxane (aluminoxane), as the catalyst system of the reactor blend polymer production. The Actual Example 1 of that Official Gazette shows that ethylene and propylene were polymerized using bis (penta methyl cyclo penta dienyl) di-methyl zirconium and alumoxane as the catalyst, and poly ethylene of which the number average molecular weight is 15,300, and the weight average molecular weight is 36,400, and which includes the propylene component at 3.4 %, was obtained. Also, the



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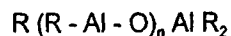
Actual Example 2 of the same Official Gazette, shows that ethylene and propylene were polymerized using bis (penta methyl cyclo penta dienyl) zirconium di-chloride and alumoxane as the catalyst, and the blend of the poly ethylene and the ethylene • propylene co-polymer of which the number average molecular weight is 2,000, and the weight average molecular weight is 8,300, and which includes the propylene component at 7.1 mole %, and which consists of a toluene soluble part of which the number average molecular weight is 2,200, and the weight average molecular weight is 11,900, and which includes the propylene component at 30 mole %, and a toluene insoluble part of which the number average molecular weight is 3,000, and the weight average molecular weight is 7,400, and which includes the propylene component at 4.8 mole %, was obtained. In the same way, Actual Example 3 of the same Gazette shows the blend material of LLDPE and ethylene • propylene co-polymer, which consists of a soluble part of which the molecular weight distribution (Mw / Mn) 4.57, and the propylene component is 20.6 mole %, and an insoluble part of which the molecular weight distribution is 3.04, and the propylene component is 2.9 mole %.

Patent Application Kokai No. S60-35007 shows the method to polymerize ethylene alone, or with an  $\alpha$ -olefin with 3 or more carbon atoms, in the presence of the catalyst system which includes metallocene, and the cyclic alumoxane that can be indicated by the following formula;



[Here, R is an alkyl group with 1 to 5 carbon atoms, n is an integer of 1 to 20.]

or the linear alumoxane that can be indicated by the following formula;



[Here, the definitions of R and n are the same as in the above description.]

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According to the description in the same Official Gazette, the polymer that is obtained by the said method, has a weight average molecular weight of about 500 to 1,400,000, and also a molecular weight distribution of 1.5 to 4.0.

Patent Application Kokai No. S60-35008 shows that poly ethylene or the co-polymer of ethylene and a  $C_3$  to  $C_{10}$  -  $\alpha$  - olefin with a wide molecular weight distribution, can be produced when the catalyst system that includes at least two or more metallocenes and alumoxane, is used in the polymerization. The same Official Gazette shows that the above mentioned co-polymer has a molecular weight distribution of ( $M_w / M_n$ ) from 2 to 50.

In addition, Patent Application Kokai No. S60-35009 shows the method to produce the co-polymer of ethylene and an  $\alpha$  - olefin in which the molecular weight distribution ( $M_w / M_n$ ) is small, less than 2, by using the catalyst system that includes a vanadium compound and an organic aluminum compound.

**[Problem That this Invention Intends to Solve]**

The objective of this invention is to offer the new low crystallinity ethylene type random co-polymer.

Another objective of this invention is to offer the ethylene type random co-polymer of which the molecular weight distribution and the composition distribution are narrow, and which has excellent transparency, excellent non-sticky surface properties, and excellent dynamic physical properties, and also which has low crystallinity.

Another objective of this invention is to offer the low crystallinity ethylene type random

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co-polymer which can give the composition with excellent impact resistance, especially the excellent low temperature impact resistance, when it is blended into the thermo plastic resin.

Another objective of this invention is to offer the low crystallinity random co-polymer which can give the composition with excellent heat sealing ability, when it is blended into the thermo plastic resin.

Another objective of this invention is to offer the low crystallinity random co-polymer which can give the composition with excellent transparency, when it is blended into the thermo plastic resin.

Another objective of this invention is to offer the method to produce the above mentioned low crystallinity ethylene type random co-polymer of this invention, and to offer the usage of it as the blending material for the thermo plastic resin.

Other objectives of this invention and the advantages of this invention will become evident from the following explanation.

#### **[Method and Operation to Solve the Problem]**

According to this invention, such objectives can be achieved by the low crystallinity ethylene type random co-polymer made from ethylene and an  $\alpha$  - olefin with 3 to 20 carbon atoms, and which is characterized by the fact that:

(a) the content of the ethylene component is in the range of 35 to 85 wt %, and the content of the  $\alpha$  - olefin component is 15 to 65 wt %;

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(b) the intrinsic viscosity  $[\eta]$  measured in decalin at 135 °C is in the range of 0.5 to 10 dL / g,;

(c) the molecular weight distribution ( $M_w / M_n$ ) obtained by gel permeation chromatography is less than 2.5,;

(d) the crystallization degree that was obtained by X - ray diffraction is 30 % or lower,;

(e) the value of B that can be indicated by the following equation (I), is in the range that it can satisfy the following equation (II),

$$B \equiv (P_{OE}) / (2 P_O \cdot P_E) \quad (I)$$

[In the equation,  $P_E$  indicates the mole ratio content of the ethylene component in the co-polymer,  $P_O$  indicates the mole ratio content of the  $\alpha$  - olefin component, and  $P_{OE}$  indicates the mole ratio of the  $\alpha$  - olefin - ethylene chain of the entire diad chain.]

$$1.05 \leq B \leq 2 \quad (II)$$

(f) in the  $^{13}\text{C}$  - NMR spectrum, the  $\alpha\beta$  signal and the  $\beta\gamma$  signal based on the methylene chain between two adjoining tertiary carbon atoms in the co-polymer main chain, can not be seen, and

(g) the part which can be dissolved in boiling methyl acetate is 2.0 wt % or less.

According to this invention, the above mentioned low crystallinity ethylene type random co-polymer of this invention, can be produced by the method in which ethylene and the  $\alpha$  - olefin with 3 to 20 carbon atoms are co-polymerized in the presence of a catalyst which consists of:

(A) a zirconium hydride compound in which the ligand is a group with a

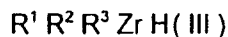
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conjugated  $\pi$  electron, and

(B) aluminoxane.

The zirconium hydride compounds (A), in which the ligand is a group with a conjugated  $\pi$  electron, are for example, the compounds that can be indicated by the following formula ( III ).



[Here,  $R^1$  indicates a cyclo alkadienyl group.  $R^2$  and  $R^3$  can be a cyclo alkadienyl group, an aryl group, an alkyl group, a halogen atom or a hydrogen atom.]

The cyclo alkadienyl groups are for example, cyclo penta dienyl groups, methyl cyclo penta dienyl groups, ethyl cyclo penta dienyl groups, di-methyl cyclo penta dienyl groups, indenyl groups, and tetra hydro indenyl groups, etc. A methyl group, an ethyl group, a propyl group, an iso propyl group, a butyl group, etc., can be listed as the alkyl group of  $R^2$  and  $R^3$ . a phenyl group, a benzyl group, a neophyl group, etc., can be listed as the aryl group. Fluorine, chlorine and bromine, etc., can be listed as the halogen. The following compounds can be listed as the said zirconium hydride compound:

bis (cyclo penta dienyl) zirconium mono chloride mono hydride,  
 bis (cyclo penta dienyl) zirconium mono bromide mono hydride,  
 bis (cyclo penta dienyl) methyl zirconium hydride,  
 bis (cyclo penta dienyl) ethyl zirconium hydride,  
 bis (cyclo penta dienyl) cyclo hexyl zirconium hydride,  
 bis (cyclo penta dienyl) phenyl zirconium hydride,  
 bis (cyclo penta dienyl) benzyl zirconium hydride,  
 bis (cyclo penta dienyl) neopentyl zirconium hydride,  
 bis (methyl cyclo penta dienyl) zirconium mono chloride mono hydride,

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and bis indenyl zirconium mono chloride mono hydride.

The above mentioned zirconium hydride compound can be used as it is, however, the compounds such as bis (cyclo penta dienyl) zirconium mono chloride mono hydride which are difficult to be dissolved in a solvent such as toluene, etc., should be preferably contacted with an organic aluminum compound, and thereafter it should be used. By this operation, the zirconium hydride compound which is difficult to dissolve in a solvent, can be made to be easily soluble.

The concrete examples of the organic aluminum compound that is supposed to be contacted with the above mentioned zirconium hydride compound, are for example, the tri alkyl aluminum such as the tri methyl aluminum, tri ethyl aluminum, and tri butyl aluminum, etc.;

tri alkenyl aluminum such as the tri isoprenyl aluminum;

di-alkyl aluminum alkoxides such as the di-methyl aluminum methoxide, di-ethyl aluminum ethoxide, and di-butyl aluminum alkoxide, etc.;

alkyl aluminum sesqui alkoxides such as the methyl aluminum sesqui methoxide, and ethyl aluminum sesqui methoxide, etc.;

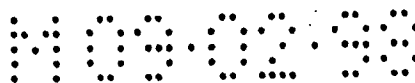
alkyl aluminum which has an average composition that can be indicated by

$R^1_{2.5}Al(OR^2)_{0.5}$ , and which is partially alkoxilated,;

di-alkyl aluminum halides such as the di-methyl aluminum chloride, di-ethyl aluminum chloride, di-methyl aluminum bromide, etc.;

alkyl aluminum sesqui halides such as methyl aluminum sesqui chloride, ethyl aluminum sesqui chloride, etc.;

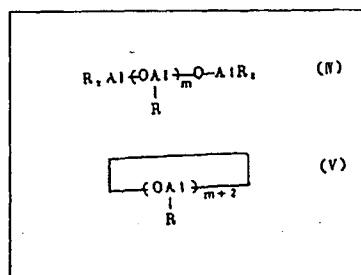
and the partially halogenated alkyl aluminum such as the alkyl aluminum di-halides, for example, methyl aluminum di-chloride and ethyl aluminum di-chloride, etc.



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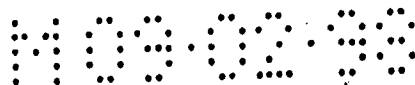
The reaction between both compounds should be performed without light and in a hydrocarbon medium. The mixing mole ratio of the organic aluminum compound and the zirconium compound, (Al / Zr), should be 0.5 to 30, preferably it should be 1 to 20. The concentration of zirconium should be maintained at 0.001 to 1 mole per 1 L of liquid phase, and preferably it should be 0.005 to 0.1 mole. The reaction temperature should be 0 to 120 °C, and under such conditions, both materials should be contacted. The above mentioned hydrocarbon medium can be selected from those which will be listed later as the solvent for polymerization.

Aluminoxane (B) which is the catalyst structural component in the method of this invention, can be an organic aluminum compound which can be indicated by the general formulas (IV) or (V).



[In the formulae, R indicates a hydrocarbon group. m indicates an integer of 20 or larger, preferably an integer of 25 or larger.]

In the said aluminoxane, R is a hydrocarbon group such as a methyl group, an ethyl group, a propyl group, or a butyl group, etc., and preferably it is a methyl group or an ethyl group, and most preferably it is a methyl group. m indicates an integer of 20 or larger, preferably 25 or larger, and most preferably it is an integer of 30 to 100. The



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following are examples of the production method of the said aluminosilicate.

(1) The method in which tri alkyl aluminum is added into the suspension liquid of the hydrocarbon medium of the compound that contains adsorbed water, the salt which contains crystal water, for example, magnesium chloride hydrate, copper sulfate hydrate, aluminum sulfate hydrate, etc., and it is reacted.

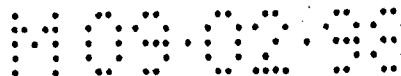
(2) The method in which the water is directly reacted with the tri alkyl aluminum in a medium such as benzene, toluene, ethyl ether, and tetra hydro furan, etc.

Among these methods, it is preferred to use method (1). The said aluminosilicate may contain a small amount of organic metal component too.

In the method of this invention, the raw materials that are fed into the polymerization reaction system is a mixture of ethylene and the  $\alpha$  - olefin with 3 to 20 carbon atoms other than ethylene. The ethylene content in the polymerization raw material olefin is normally 10 to 90 mole %, preferably it should be 20 to 80 mole %, and the content of the said  $\alpha$  - olefin is normally 10 to 90 mole %, preferably it should be in the range of 20 to 80 mole %.

The concrete examples of an  $\alpha$  - olefin with 3 to 20 carbon atoms other than ethylene that are used as the polymerization raw materials in this invention, are, propylene, 1-butene, 1-hexene, 4-methyl-1-pentene, 1-octene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, 1-octadecene, and 1-eicosane, etc.

In the method of this invention, the polymerization reaction of olefin is normally carried out in a hydrocarbon medium. To be concrete, the hydrocarbon medium is an aliphatic hydrocarbon such as butane, iso butane, pentane, hexane, octane, decane, dodecane,



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hexa decane, octa decane, etc.;

an alicyclic hydrocarbon such as cyclo pentane, methyl cyclo pentane, cyclo hexane, cyclo octane, etc.;

an aromatic hydrocarbon such as benzene, toluene, xylene, etc.;

a petroleum distillate portion such as gasoline, kerosine, light oil, etc.;

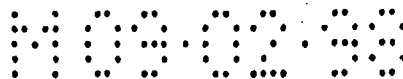
and in addition, the raw material olefin can be the hydrocarbon medium too. Among these hydrocarbon media, the aromatic hydrocarbons are preferred.

The liquid phase polymerization methods such as the suspension polymerization method, the solution polymerization method, etc., are normally applied as the method of this invention, and especially the solution polymerization method is suitably applied.

The temperature of the polymerization reaction should be -50 to 200 °C, preferably it should be in the range of -20 to 80 °C.

When the method of this invention is practiced using the liquid phase polymerization method, the amount of the said zirconium hydride compound (A) to be used should be normally  $10^{-8}$  to  $10^{-2}$  gram atom / L as the concentration of the zirconium metal atoms in the polymerization reaction system, and preferably it should be in the range of  $10^{-7}$  to  $10^{-3}$  gram atom / L. The amount of the aluminoxane to be used should be normally  $10^{-4}$  to  $10^{-1}$  gram atom / L as the concentration of the aluminum atoms in the polymerization reaction system, and preferably it should be in the range of  $10^{-3}$  to  $5 \times 10^{-2}$  gram atom / L. The ratio of the aluminum metal atoms to the zirconium metal atoms in the polymerization reaction system should be normally 25 to  $10^7$ , preferably it should be in the range of  $10^2$  to  $10^8$ . The molecular weight of the co-polymer can be adjusted by the hydrogen and / or polymerization temperature.

In the method of this invention, after the polymerization reaction is completed, the



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polymerization reaction mixture is treated by normal methods, and thus, the above mentioned low crystallinity ethylene type co-polymer of this invention can be obtained.

The composition of the low crystallinity ethylene type co-polymer of this invention is such that the ethylene component is 35 to 85 wt %, preferably 40 to 80 wt %, and the said  $\alpha$  - olefin component is 15 to 65 wt %, preferably in the range of 20 to 60 wt %.

Also, the low crystallinity ethylene type random co-polymer of this invention normally has an intrinsic viscosity value  $[\eta]$  of 0.5 to 10 dL / g, preferably in the range of 1 to 6 dL / g, when it is measured in decalin at 135 °C.

Also, the molecular weight distribution ( $M_w / M_n$ ) of the said low crystallinity ethylene type co-polymer of this invention measured by gel permeation chromatography (GPC) is less than 2.5, preferably 2.3 or less, and more preferably it should be 2 or less. If the molecular weight distribution of the said low crystallinity ethylene type co-polymer is greater than 2.5, the said co-polymer or the composition in which the said co-polymer was blended as the reforming agent, becomes sticky, or it causes blocking, therefore, it is necessary to be in the above mentioned range.

The said low crystallinity ethylene type co-polymer has low crystallinity, and the crystallization degree obtained by X-ray diffraction is less than 30 %, preferably less than 20 %, and more preferably it is in the range of 0 to 15 %.

The measuring of the  $M_w / M_n$  value can be done as follows, according to "Gel Permeation Chromatography" written by Takeuchi and published by Maruzen K.K.

(1) Using the standard poly styrene (mono dispersed poly styrene made by Toyo Soda K.K.) of which the molecular weight is known, the molecular weight  $M$  and the GPC (Gel

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Permeation Chromatography) counts were measured, and the correlation calibration curve of the molecular weight  $M$  and the EV (elution volume) is made. The concentration at this time should be 0.02 wt %.

(2) The GPC chromatograph of sample is made by obtaining the GPC, and from the above mentioned (1), the number average molecular weight  $M_n$  converted to polystyrene and the weight average molecular weight  $M_w$  were calculated, and the value of  $M_w / M_n$  is obtained. The sample preparation conditions at that time, and the GPC measuring conditions are listed below.

**[Sample Preparation]**

☐ Sample is dispersed into a flat bottom flask with O- di-chloro benzene to make an 0.1 wt % solution.

☐ 2, 6 - di- tert - butyl -p- creosol, which is the aging prevention agent, is added into the flask in which the sample is contained, to make 0.05 wt % of the polymer solution.

☐ The flask is heated to 140 °C, and it is stirred for about 30 minutes, and it is dissolved.

☐ The filtrate of this is used for GPC.

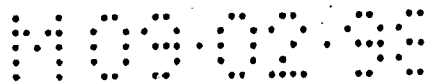
**[Gpc Measuring Conditions]**

This was carried out under the following conditions.

☐ Device : (150C - ALC / GPC) made by Waters Co.

☐ Column : (GMH type) made by Toyo Soda K.K.

☐ Amount of sample : 400  $\mu$ L



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( ) Temperature : 140 °C

( ) Flow rate : 1 mL / min.

In addition, in the low crystallinity ethylene type co-polymer of this invention, the value of B that can be indicated by the following equation ( I ), is in the range where it can satisfy the following equation ( II ),

$$B \equiv (P_{OE}) / (2 P_O \cdot P_E) \quad (I)$$

[In the equation,  $P_E$  indicates the mole ratio content of the ethylene component in the co-polymer,  $P_O$  indicates the mole ratio content of  $\alpha$  - olefin component, and  $P_{OE}$  indicates the mole ratio of the  $\alpha$  - olefin · ethylene chain of the entire diad chain.]

$$1.05 \leq B \leq 2 \quad (II)$$

The above mentioned value B is an indicator that indicates the distribution of each monomer component in the co-polymer chain, and it can be calculated by obtaining  $P_E$ ,  $P_O$ , and  $P_{OE}$  of the above definitions, based on the reports such as

G. J. Ray (Macromolecules, 10, 773 (1977))

J. C. Randall (Macromolecules, 15, 353 (1982))

J. Polymer Science, Polymer Physics Ed., 11, 275 (1973))

and K. Kimura (Polymer, 25, 441, (1984)).

The larger the above mentioned B value is, the lesser the block type chain is, and it indicates that it is the co-polymer in which the distribution of ethylene and the  $\alpha$  - olefin is even, and the composition distribution is narrow.

The low crystallinity ethylene type co-polymer of this invention preferably has the B value indicated below.

In the case when the ethylene content of the co-polymer is 50 mole % or less:

$$1.0 + 0.3 \times P_E \leq B \leq 1 / (1 - P_E)$$

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More preferably,  $1.0 + 0.4 \times P_E \leq B \leq 1 / (1 - P_E)$ .

Most preferably,  $1.0 + 0.5 \times P_E \leq B \leq 1 / (1 - P_E)$ .

In the case when the ethylene content of the co-polymer is 50 mole % or higher:

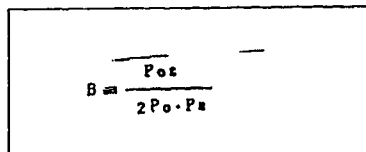
$1.3 - 0.3 \times P_E \leq B \leq 1 / P_E$ .

More preferably,  $1.4 - 0.4 \times P_E \leq B \leq 1 / P_E$ .

Most preferably,  $1.5 - 0.5 \times P_E \leq B \leq 1 / P_E$ .

By the way, in order to obtain the composition distribution B value, about 200 mg of co-polymer was evenly dissolved in 1 mL of hexa chloro butadiene in a 10 mm  $\phi$  sample tube, and the  $^{13}\text{C}$  - NMR spectrum of this sample was measured under the following measuring conditions: a temperature of 120 ° C, a measuring frequency of 25.05 MHz, a spectrum width of 1500 Hz, a filter width of 1500 Hz, a pulse repeat time of 4.2 sec., a pulse width of 7  $\mu\text{sec}$ , and a total repeating number of 2000 to 5000 times. From this spectrum,  $P_E$ ,  $P_O$  and  $P_{OE}$  were obtained, and then B was calculated. In addition, the  $\alpha\beta$  signal and the  $\beta\gamma$  signal based on the methylene chain between the two adjoining tertiary carbon atoms in the co-polymer main chain, can not be seen in the  $^{13}\text{C}$  - NMR spectrum of the low crystallinity ethylene type co-polymer of this invention. For example, in the below

polymer of ethylene



listed bond in the co-  
and 1 - hexene,

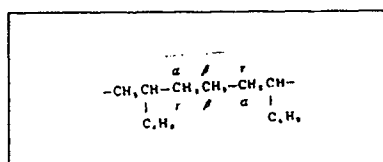
the three methylene groups in the middle are in the  $\alpha$ ,  $\beta$ ,  $\gamma$  positions from the left when it is seen from the tertiary carbon on the left side from the 1 - hexene. On the other hand,

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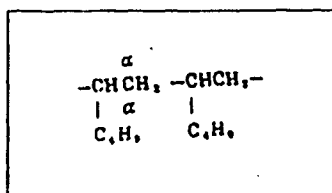
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when it is seen from the tertiary carbon on the right side, it is the  $\alpha$ ,  $\beta$ ,  $\gamma$  position from the right side. Therefore, there is a methylene group that gives an  $\alpha\gamma$  signal and a  $\beta\beta$  signal, however, there is no methylene group that gives a  $\alpha\beta$  signal and a  $\beta\gamma$  signal in the above mentioned bond unit.

In the same manner as above, in the below listed bond in which the 1 - hexene and 1 - hexene are bonded at the head and tail,



there is only a methylene group that gives an  $\alpha\alpha$  signal, and there is no methylene group that gives an  $\alpha\beta$  signal or a  $\beta\gamma$  signal.



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$$\begin{array}{c} \text{a} \quad \beta \quad \gamma \quad \delta \\ \text{---CHCH}_2\text{---CH}_2\text{CH}_2\text{---CH}_2\text{CH---} \rightarrow \text{I CF} \\ | \quad \quad | \quad \quad | \\ \text{C}_6\text{H}_5 \quad \quad \text{C}_6\text{H}_5 \end{array}$$

The boiling methyl acetate soluble part of the low crystallinity ethylene type random co-polymer of this invention is 2 wt % or less, preferably it should be 1.5 to 0.01 wt %, more preferably it should be 1.0 to 0.03 wt %, and most preferably it should be in the range of 0.7 to 0.05 wt %. When the weight ratio of the ethylene component unit in the low crystallinity ethylene type random co-polymer is  $P_{EW}$ , the boiling methyl acetate soluble part [ $E_x$  wt %] of the low crystallinity ethylene type random co-polymer should be in the following range;

$$E_x \leq 2.2 - 2 \times P_{EW}$$

Preferably,  $E_x \leq 1.35 - P_{EW}$

More preferably,  $E_x \leq 0.9 - 0.6 \times P_{EW}$

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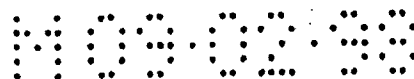
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made into a 1 mm thick pressed sheet, and this pressed sheet was cut into a 2 mm x 2 mm square, and this was put into a cylindrical glass filter, and it was extracted using a Soxhlet extractor for 6 hours with a reflux frequency of about once every 5 minutes. The extraction amount was obtained by drying the extracted residue in a vacuum dryer until the weight became constant.

The low crystallinity ethylene type random co-polymer of this invention normally has a density of 0.90 g/cc or less. The breakage point stress and the breakage point elongation are each 300 kg / cm<sup>2</sup> or less, and 400 % or higher, respectively. Here, the density was measured after the sample was heat treated at 120 °C for 1 hour and then it was cooled to room temperature over a period of 1 hour. In order to measure the breakage point stress and the breakage point elongation, a ring shaped test specimen (an inner diameter of 18 mm, an outer diameter of 22 mm and a thickness of 1 mm) was made, and it was measured with a pulling speed of 500 mm / min at a measuring temperature of 25 °C.

Compared with the co-polymer that was obtained using the titanium type catalyst, the low crystallinity ethylene type random co-polymer of this invention has a narrow molecular weight distribution and a narrow composition distribution, and also it has excellent transparency, non-stickiness of the surface and excellent dynamic physical properties. Compared with the co-polymer that was obtained using the vanadium type catalyst, the molecular weight distribution and the composition distribution are about equal or narrower, but the configuration of the co-polymer component in the molecular chain is different.

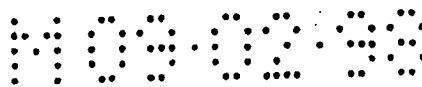
The low crystallinity ethylene type random co-polymer of this invention can be blended into various thermo plastic resins as the reformer.



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When the low crystallinity ethylene type random co-polymer of this invention is blended into another ethylene type polymer such as poly ethylene which includes ethylene as the main component, the ethylene type polymer composition in which the impact resistance, especially the low temperature impact resistance, the bend resistance, and the low temperature heat seal ability are improved, can be obtained. In addition, even though the low crystallinity ethylene type random co-polymer was added, the transparency or the non-stickiness of surface of the said ethylene type polymer composition do not deteriorate. The other above mentioned ethylene type polymers are, for example, the high density poly ethylene, the middle density poly ethylene, low density poly ethylene, ethylene and propylene, and the co-polymers with an  $\alpha$  - olefin with 3 to 20 carbon atoms such as 1 - butene, 1- hexene, 4 - methyl -1- pentene, 1 - octene, 1- decene, 1 - dodecene, 1- tetra decene, 1- hexa decene, 1- octa decene, 1 - eicosane, etc., and which are the ethylene type co-polymers which include ethylene as their main component. The intrinsic viscosity  $[\eta]$  measured in decalin at 135 °C should be in the range of 0.5 to 20 dL / g.

In the case when the low crystallinity ethylene type random co-polymer of this invention is going to be added into another ethylene type polymer, the blending ratio should be normally 0.5 to 30 weight parts per 100 weight parts of the other ethylene type polymer, preferably it should be in the range of 1 to 20 weight parts. If necessary, various additives such as an oxidation preventor, a hydrochloric acid absorber, an agglomeration preventor, a heat resistance stabilizer, a UV absorber, a slip additive, weather resistance stabilizers, anti static agents, a nucleation agent, pigments, fillers, etc., can be also added into the polymer composition that is obtained. The added amount of these should be appropriate. The said ethylene type polymer composition can be prepared by the methods that have been known until now.



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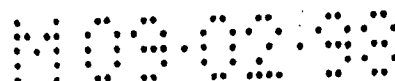
Also, when the low crystallinity ethylene type random co-polymer of this invention is ~~blended~~ into the crystalline olefin type polymer other than the above mentioned other ethylene type polymer, the formed product made out of the said crystalline olefin type polymer has the *(here, words are missing, but it must mean improved impact resistance, Translator)*, especially at low temperatures. In addition, even though the said low crystallinity ethylene type random co-polymer was added, the transparency or the non-stickiness of surface characteristically do not deteriorate. The crystalline olefin type polymers other than the said ethylene type polymer, are, for example, ~~poly~~ ~~propylene~~, poly -1 - butene, poly -4 - methyl -1- pentene, poly -1- hexene, etc., and in addition, the crystalline  $\alpha$  - olefin type co-polymers such as the propylene • ethylene co-polymer, propylene • 1 - butene co-polymer, 1- butene • ethylene co-polymer, 1- butene • propylene co-polymer, etc., which consists of :  
 $\alpha$  -olefin ( $a_1$ ) such as propylene, 1- butene, 1 - hexene, etc., and  
 $\alpha$  -olefin ( $a_2$ ) which is an  $\alpha$  - olefin with 2 to 20 carbon atoms such as ethylene, propylene, 1 - butene, 1 - hexene, 4- methyl -1- pentene, 1 - octene, 1- decene, 1 - dodecene, 1- tetra decene, 1- hexa decene, 1- octa decene, 1 - eicosane, etc., and which are different from the above mentioned  $\alpha$  -olefin ( $a_1$ ). The intrinsic viscosity  $[\eta]$  of the said crystalline olefin type polymer measured in decalin at 135 °C is normally in the range of 0.5 to 10 dL / g, and the crystallization degree should be 5 % or higher, preferably it should be 20 % or higher.

In the case when the low crystallinity ethylene type random co-polymer of this invention is going to be added into the said crystalline  $\alpha$  - olefin type polymer, the blending ratio should be normally 0.5 to 30 weight parts per 100 weight parts of the said crystalline  $\alpha$  - olefin type polymer, preferably it should be in the range of 1 to 20 weight parts. If necessary, various additives such as an oxidation preventor, a hydrochloric acid absorber, an agglomeration preventor, a heat resistance stabilizer, a UV absorber, a

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slip additive, weather resistance stabilizers, anti static agents, a nucleation agent, pigments, fillers, etc., can be also added into the said crystalline  $\alpha$  - olefin type polymer composition. The said crystalline  $\alpha$  - olefin type polymer composition can be prepared by the methods that have been known until now.

In addition when the low crystallinity ethylene type random co-polymer of this invention is added into the various engineering resins, the physical properties of the engineering resin, for example, the impact resistance, the slide characteristics, etc., can be improved, and in addition, even though the low crystallinity ethylene type random co-polymer was added, the transparency or the non-stickiness of surface do not deteriorate. In the case when the said engineering resin has a polar group, in order to improve the affinity or the dispersion ability into the said engineering resin, it is preferred to use the modified ethylene type random co-polymer in which an unsaturated carboxylic acid or its derivative component, such as maleic acid, citraconinc acid, itaconic acid, maleic anhydride, citraconic anhydride, itaconic anhydride, di-methyl maleate, di-methyl citraconate, di-methyl itaconate, etc., is graft polymerized in the low crystallinity ethylene type random co-polymer of this invention. The grafting ratio of the said unsaturated di-carboxylic acid or its derivative component should be normally 0.02 to 50 weight parts per 100 weight parts of the said low crystallinity ethylene type random co-polymer. The engineering resins are for example, the poly esters such as poly ethylene tere phthalate, poly butylene tere phthalate, etc.,; poly amides such as hexa methylene adipamide, octa methylene adipamide, deca methylene adipamide, dodeca methylene adipamide, poly capro lactone, etc.; poly aryene oxides such as poly phenylene oxide, etc.,; and poly acetals, ABS, AES, and poly carbonates, etc. The blending ratio of the said low crystallinity ethylene type random co-polymer or its modified material should be normally 0.2 to 20 weight parts per 100 weight parts of the said engineering resin. If necessary, various additives such as an oxidation preventor,



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a hydrochloric acid absorber, an agglomeration preventor, a heat resistance stabilizer, a UV absorber, a slip additive, weather resistance stabilizers, anti static agents, a nucleation agent, pigments, fillers, etc., can be also added into the said engineering resin composition. The said engineering resin composition also can be prepared by the methods that have been known until now.

When the low crystallinity ethylene type random co-polymer of this invention is added into the various rubber like polymers, the physical properties of the said rubber like polymer, for example, the chemical resistance, the rigidity, etc., can be improved. The said rubber like polymers are for example, ethylene • propylene • non conjugated diene co-polymer, ethylene • 1 - butene • non conjugated diene co-polymer, poly butadiene rubber, poly isoprene rubber, and the styrene • butadiene • styrene block co-polymer, etc. The blending ratio of the said low crystallinity ethylene type random co-polymer should be normally in the range of 1 to 100 weight parts per 100 weight parts of the above mentioned rubber like polymer. If necessary, the various additives such as a filler, a cross linking agent, a cross linking assist agent, pigments, stabilizers, etc., can be added into the said rubber like polymer composition. The said rubber like polymer composition can be prepared by the methods that have been known until now.

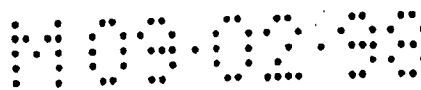
#### [Actual Examples]

Next, this invention will be explained concretely referring to actual examples.

#### **Actual Example 1**

##### **Preparation of zirconium catalyst**

30 mL of toluene and 2 milli moles of bis (cyclo penta dienyl) zirconium mono chloride mono hydride were put into a 100 mL glass flask which had already been purged sufficiently with nitrogen, and it was made into a slurry. 20 milli moles of toluene -



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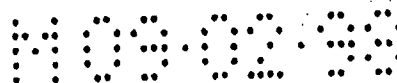
diluted - tri methyl aluminum (1 M solution) was dropped into this at room temperature. After the dropping was completed, the temperature was increased to 60 °C, and it was reacted for 1 hour. Bis (cyclo penta dienyl) zirconium mono chloride mono hydride was dissolved in toluene, and the solution became dark red in color. Here, this reaction was performed while blocking the light.

**Preparation of methyl aluminoxane** (*The original says amino oxane but this must be a typo of aluminoxane, Translator*)

125 mL of toluene and 13.9 g of magnesium chloride hexa hydrate were put into a 400 mL glass flask which had already been purged sufficiently with argon, and it was cooled to 0 °C. Thereafter, 250 milli moles of tri methyl aluminum that had been diluted with 125 mL of toluene, was dropped into this. After the dropping was completed, the temperature was increased to 70 °C, and it was reacted for 96 hours at that temperature. After the reaction was finished, the solid and the liquid were separated by filtration, and the toluene was removed from the separated liquid under reduced pressure, and 7.3 g of white solid methyl aluminoxane was obtained. The molecular weight that was obtained by the freezing point depression in benzene was 1910, and the m value of the said aluminoxane was 31. Here, the above mentioned aluminoxane was re-dissolved in toluene and this was used during the polymerization time.

#### **Polymerization**

Using a 2 L - continuous polymerization reactor, purified toluene was continuously fed at a rate of 2 L / hr, methyl aluminoxane was fed at a rate of 10 mg atom / hr converted to atomic aluminum, and the above mentioned zirconium catalyst was fed continuously at a rate of  $1 \times 10^{-2}$  mg atom / hr converted to atomic zirconium into the reactor. At the same time, ethylene (360 L / hr) and 1 - butene (240 L / hr) were continuously fed into the reactor in this ratio, and the polymerization was performed under the conditions of a



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polymerization temperature of 20 °C, normal pressure, a residence time of 0.5 hour, and the conditions under which the polymer concentration became 36 g / L. The polymer solution that was formed, was continuously taken out from the reactor, and the polymerization was stopped by adding a small amount of methanol. Then, this polymer solution was transferred into a large amount of methanol, and the polymer that was precipitated was dried under reduced pressure at 130 °C for 12 hours. The rubber like polymer that was obtained contained 77 wt % of ethylene.  $[\eta]$  was 2.16 dL / g.  $M_w / M_n$  was 1.85. The crystallization degree was 21 %. The B value was 1.14, and the density was 0.888 g / cm<sup>3</sup>, and the amount extracted in boiling methyl acetate was 0.31 wt %. The breakage point stress of this polymer was 110 kg / cm<sup>2</sup>, and the breakage point elongation was 900 %. The signals based on  $\alpha\beta$  and  $\beta\gamma$  were not detected in the <sup>13</sup>C - NMR spectrum of this obtained polymer. The unit activity of the zirconium was 7300 g polymer / mg atom - Zr.

#### **Actual Examples 2 to 8, and Comparison Example 1**

These were performed the same as in Actual Example 1, except that it was polymerized under the conditions indicated in Table 1. The signal based on  $\alpha\beta$  and  $\beta\gamma$  were not detected in the <sup>13</sup>C - NMR spectrum of the obtained polymers. The results are shown in Table 1.

#### **Comparison Example 2**

##### **Preparation of titanium catalyst**

2 g of tetra butoxy titanium and 20 g of magnesium chloride anhydride were put into a 800 mL - SUS "Porato" (*this may be a typo of "pot", Translator*) which included 2.8 kg of SUS balls (15 mm  $\phi$ ), and it was crushed for 8 hours (vibration mill) under a nitrogen atmosphere. The crushed material was transferred into 200 mL of ethylene chloride, and it was heated to 80 °C for 2 hours. Thereafter, the crushed material was filtered,

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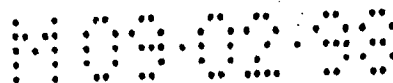
and it was washed with n- decane, until the free titanium tetra chloride could not be detected any more. 21 mg of atomic titanium was supported on 1 g of catalyst prepared like this.

#### **Polymerization**

Using the same polymerization reactor as in Actual example 1, purified decane was continuously fed at a rate of 2 L / hr, ethyl aluminum sesqui chloride was fed at a rate of 8 mg atom / hr converted to atomic aluminum, and the above mentioned titanium catalyst was fed continuously at a rate of 0.4 mg atom / hr converted to atomic titanium into the reactor. At the same time, ethylene (300 L / hr) and 1 - butene (100 L / hr) were continuously fed into the reactor in this ratio, and the polymerization was performed under the conditions of a polymerization temperature of 120 °C, normal pressure, a residence time of 0.5 hour, and the conditions under which the polymer concentration became 50 g / L. The subsequent operation was the same as that in Actual Example 1. The obtained polymer did not show a signal based on  $\alpha\beta$  and  $\beta\gamma$  in the  $^{13}\text{C}$  - NMR spectrum. The results are shown in Table 2.

#### **Comparison Example 3**

Using the same polymerization reactor as that in Actual example 1, purified hexane was continuously fed at a rate of 2 L / hr, ethyl aluminum sesqui chloride was fed at a rate of 1 mg atom / hr converted to atomic aluminum, and the vanadyl tri chloride was fed continuously at a rate of 0.1 mg atom / hr converted to atomic vanadium into the reactor. At the same time, ethylene (200 L / hr) and propylene (240 L / hr) were continuously fed into the reactor in this ratio, and the polymerization was performed under the conditions of a polymerization temperature of 50 °C, normal pressure, a residence time of 0.5 hour, and the conditions under which the polymer concentration became 4 g / L. The subsequent operation was the same as that in Actual example 1. Being different from the Actual Examples 1 to 8, the obtained polymer showed a signal



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based on  $\alpha\beta$  and  $\beta\gamma$  in the  $^{13}\text{C}$  - NMR spectrum. The results are shown in Table 3.

#### **Comparison Examples 4 to 6**

These were performed the same as in Comparison Example 3 except that they were polymerized under the conditions indicated in Table 3. Being the same as Comparison Example 3, the obtained polymers showed the signals based on  $\alpha\beta$  and  $\beta\gamma$  in the  $^{13}\text{C}$  - NMR spectra. The results are shown in Table 3.

#### **Applied Examples 1 to 5, and Comparison applied examples 1 to 6**

The ethylene type random co-polymer of the above mentioned Actual Examples and Comparison Examples, and the poly ethylene resin (MFR 0.44 g / 10 min, density of 0.959 g / cm<sup>3</sup>) were melt - mixed at a ratio of 1 : 9, and thereafter, a 70  $\mu\text{m}$  thick press film was made (180 °C, preheat for 5 minutes → gas removal for 30 seconds → pressurization at 30 kg / cm<sup>2</sup>, maintaining for 4 min 30 sec. → 20 °C cold press, pressurization at 50 kg / cm<sup>2</sup>, maintaining for 3 min). The film impact strength of this film and the transparency (haze value) were measured at 23 °C and at -20 °C. The results are shown in Table 4.

#### **Applied Example 6, and Comparison Applied Examples 7 to 9**

The ethylene type random co-polymer of the above mentioned Actual Examples and Comparison Examples, and the poly propylene resin (MFR 10 g / 10 min) were melt - mixed in the ratio of 1 : 9, and thereafter, a 30  $\mu\text{m}$  thick press film was made (the same as in Applied Example 1). The film impact strength of this film and the transparency (haze value) were measured at 23 °C. The results are shown in Table 5.

#### **Actual Example 11**

##### **Preparation of the zirconium catalyst**

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This was carried out the same as in Actual Example 1, except that tri n-octyl aluminum was used instead of the tri methyl aluminum that was used in Actual Example 1.

### Polymerization

Using the same polymerization reactor as in Actual Example 1, purified toluene was continuously fed at a rate of 1 L / hr, methyl aluminoxane that was synthesized the same as that in Actual Example 1 was fed at a rate of 5 mg atom / hr converted to atomic aluminum, and the above mentioned zirconium catalyst was fed continuously at a rate of  $1 \times 10^{-2}$  mg atom / hr converted to atomic zirconium into the reactor. At the same time, ethylene (at 360 L / hr), propylene (at 240 L / hr) and 1, 4 - hexa diene (at 2 g / hr) were continuously fed into the reactor in this ratio, and the polymerization was performed under the conditions of a polymerization temperature of 20 °C, normal pressure, a residence time of 1 hour, and the conditions under which the polymer concentration became 20 g / L. The subsequent operation was the same as that in Actual Example 1. The rubber like polymer that was obtained contained 70 wt % of ethylene.  $[\eta]$  was 1.79 dL / g.  $M_w / M_n$  was 1.92. The crystallization degree was 0 %. The B value was 1.19, and the density was 0.871 g / cm<sup>3</sup>. The iodine value was 9, and the amount extracted in boiling methyl acetate was 0.38 wt %. The signals based on  $\alpha\beta$  and  $\beta\gamma$  were not detected in the <sup>13</sup>C - NMR spectrum of this polymer. The unit activity of the zirconium was 2000 g - polymer / mg atom - Zr.

Table 1

	Monomer 1		Monomer 2		Polymeri. temp.	Polymer conc.	Activity	Ethylene content
	Type	(L / hr)	Type	(L / hr)	(°C)	(g / L)	(***)	(wt %)
Ac. Ex 1	Ethylene	360	1 - butene	240	20	36	7,300	77
Ac. Ex 2	Ethylene	300	1 - butene	300	20	35	6,900	69
Ac. Ex 3	Ethylene	240	1 - butene	360	20	41	8,100	60

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Ac. Ex 4	Ethylene	360	1 - butene	240	0	29	5,700	65
Ac. Ex 5	Ethylene	360	1- hexene	0.3	20	47	9,400	69
Ac. Ex 6	Ethylene	360	1- hexene	0.6	20	34	6,800	57
Ac. Ex 7*	Ethylene	360	1- hexene	0.2	40	41	16,200	79
Ac. Ex 8	Ethylene	360	4- MP-1 **	0.6	20	24	4,700	77
Co. Ex 1*	Ethylene	450	Propylene	150	30	36	14,300	87

Ac. Ex means Actual Example.

Co. Ex means Comparison Example.

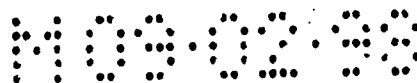
Polymeri. Temp. means Polymerization temperature.

conc. means concentration.

(\*\*\*) : g • polymer / mg atom • Zr

(common polymerization conditions) : solvent 2 L / hr, Zr  $5 \times 10^{-7}$  mg atom / L (\*  $2.5 \times 10^{27}$ ) Al 5 mg atom / L, residence time 0.5 hr

\*\* : 4- methyl pentene -1



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Table 1 continued:

	$[\eta]$ (dL / g)	Mw/Mn	Crystallization Degree (%)	B value	Density (g / cm <sup>3</sup> )	Br. Point Stress. (kg / cm <sup>2</sup> )	Br. Point elongation (%)	Appearance (stickiness)	(****) (wt %)
Ac. Ex 1	2.16	1.85	21	1.14	0.888	110	900	nothing	0.31
Ac. Ex 2	1.87	1.88	0	1.18	0.877	30	960	nothing	0.35
Ac. Ex 3	1.54	1.91	0	1.23	0.865	-	-	nothing	0.39
Ac. Ex 4	4.10	1.94	0	1.20	0.872	15	990	nothing	0.33
Ac. Ex 5	2.03	1.91	0	1.16	0.875	175	700	nothing	0.34
Ac. Ex 6	1.36	1.84	0	1.21	0.861	120	810	nothing	0.42
Ac. Ex 7*	1.99	1.93	2.3	1.08	0.890	210	750	nothing	0.27
Ac. Ex 8	1.30	1.94	0.5	1.07	0.887	195	600	nothing	0.30
Co. Ex 1*	2.51	2.12	35	1.09	0.904	90	710	nothing	0.25

Br. Point means Breakage point.

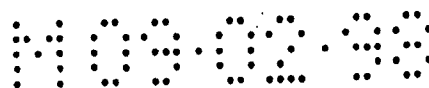
(\*\*\*\*) : amount extracted in boiling methyl acetate

Table 2

	Activity (g . polymer / mg . Ti)	Ethylene content (wt %)	$[\eta]$ (dL / g)	Mw / Mn	Crystallization degree (5)	B value	Density (g / cm <sup>3</sup> )	Br. Point. Stress. (kg / cm <sup>2</sup> )
Co. Ex. 2	250	75	1.35	4.68	14.3	0.92	0.889	60

Continued

Breakage point elongation (%)	Appearance (stickiness)	Boiling methyl acetate extraction amount (wt %)
1050	stickiness exists	1.53



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Table 3

	Monomer 1		Monomer 2		V (mg atom / L)	Al (mg atom / L)	Polymeri Temp. (°C)	Polyme r conc. (g / L)	Activity (g.polymer / mg atom.V)
	Type	(L / hr)	Type	(L / hr)					
Co, Ex. 3	Ethylene	200	Propylene	240	0.05	0.5	50	4	80
Co, Ex 4	Ethylene	240	1 - butene	160	0.4	4.0 *	40	41	100
Co, Ex 5	Ethylene	200	1 - hexene	0.4	0.5 **	5.0	20	65	130
Co, Ex 6	Ethylene	200	4 - MP -1	0.4	0.5 **	5.0	20	35	70

Co. Ex means Comparison Example.

Polymeri. Temp. means Polymerization temperature.

conc. means concentration.

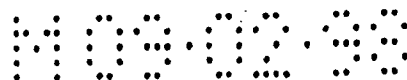
\* :  $\text{Et}_2\text{AlCl} / \text{Et}_7\text{AlCl}_{1.57} = 1 / 1$  m. r.

\*\* :  $\text{VO}(\text{OEt})\text{Cl}_2$  was used.

Table 3 continued:

	Ethylene content (wt %)	[ $\eta$ ] (dL / g)	Mw / Mn	Crystalli zation degree (%)	B value	Density (g / cm <sup>3</sup> )	Br. point stress (Kg / cm <sup>2</sup> )	Br. point elongation (%)	Appearance (stickiness)	Boiling methyl acetate extraction amount (wt %)	remark
Co. Ex 3	67	2.29	2.29	0	1.11	0.867	15	1000	slightly exists	0.80	
Co. Ex 4	82	1.50	2.41	17.9	1.07	0.890	145	890	slightly exists	0.45	-
Co. Ex 5	54	1.86	2.37	0	1.11	0.857	-	-	slightly exists	0.65	
Co. Ex 6	71	1.52	2.32	0	1.08	0.868	115	930	slightly exists	0.51	

\* :  $\text{H}_2$  was supplied at 20 L / hr.



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**Table 4**

	Ethylene type random co-polymer	Blended material				
		MFR (g / 10 min)	density (g / cm <sup>3</sup> )	Film impact strength (kg.cm / cm)		Haze (%)
				23 °C	- 20 °C	
Ap. Ex. 1	Ac.Ex. 1	0.51	0.950	1710	1750	32
Ap. Ex. 2	Ac.Ex. 3	0.56	0.947	2320	2620	35
Ap. Ex. 3	Ac.Ex. 5	0.51	0.948	2430	2300	33
Ap. Ex. 4	Ac.Ex. 6	0.64	0.945	2540	2560	34
Ap. Ex. 5	Ac.Ex. 8	0.66	0.950	2090	2110	35
Co. Ap. Ex. 1	Co, Ex 1	0.46	0.953	1320	1290	33
Co. Ap. Ex 2	Co, Ex 2	0.58	0.950	1310	1350	51
Co. Ap. Ex 3	Co, Ex 3	0.45	0.948	1560	1760	47
Co. Ap. Ex 4	Co, Ex 4	0.56	0.951	1510	1540	39
Co. Ap. Ex 5	Co, Ex 5	0.53	0.944	2210	2300	44
Co. Ap. Ex 6	Co, Ex 6	0.56	0.948	2000	2050	40
	Base polymer	0.44	0.959	1120	1120	31

Ap. Ex means Applied Example.

Co. Ap. Ex means Comparison applied example.

**Table 5**

	Ethylene type random co-polymer	Blended material		
		MFR (g / 10 min)	Film impact strength (kg. cm / cm)	Haze (%)
Ap. Ex. 6	Ac.Ex. 1	9	2100	4
Co. Ap. Ex. 7	Co, Ex 2	10	1600	12

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Co. Ap. Ex 8	Co, Ex 3	9	1900	10
Co. Ap. Ex 9	Co, Ex 4	10	1900	6
Base polymer	-	10	1400	3

Ap. Ex means Applied Example.

Co. Ap. Ex means Comparison applied example.

Ac. Ex means Actual example.

Co. Ex means Comparison example.

#### [Effect of the Invention]

As was mentioned above, the low crystallinity ethylene type random co-polymer of this invention has a narrow molecular weight distribution and a narrow composition distribution, and it has excellent transparency, and it does not have a sticky surface, and it has a low degree of crystallinity.

When the above mentioned co-polymer of this invention is added into the thermo plastic resin, the various natures of the said resin can be improved.

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